Accessory Publication for:

# A butterfly-shaped water tetramer in a Cu₄ complex supported by a hydrazone ligand: Synthesis, crystal structure, magnetic properties and quantum chemical study

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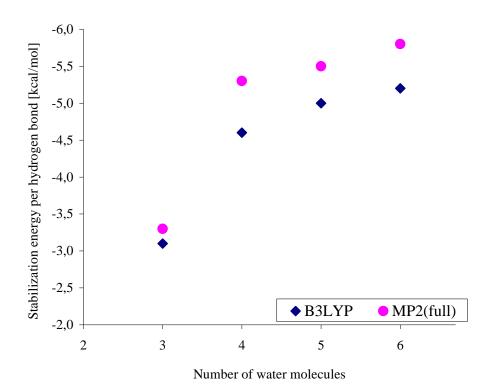[e] Computer Chemistry Center, Department of Chemistry and Pharmacy, University of Erlangen-Nürnberg, Nägelsbachstr 25, 91052 Erlangen, Germany.

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Table S1: Calculated stabilization energy per hydrogen bond of the water cluster

| [kcal/mol] | B3LYP | MP2(full) | d(H···O) [Å] |
|---|---|---|---|
| Trimer | -3.1 | -3.3 | 1.91 |
| Tetramer | -4.6 | -5.3 | 1.78 |
| Pentamer | -5.0 | -5.5 | 1.75 |
| Hexamer | -5.2 | -5.8 | 1.74 |

B3LYP: B3LYP/6-311+G(3df,2p) + ZPE(B3LYP/6-311+G(3df,2p))
MP2(full): MP2(full)/6-311+G(3df,2p)//B3LYP/6-311+G(3df,2p) + ZPE(B3LYP/6-311+G(3df,2p))
d(H···O):  distances of the hydrogen bonds in the water cluster

Scheme S1: Calculated stabilization energy per hydrogen bond compared with the
Number of water molecules in the cyclic structure.

**Gaussian summaries for the discussed structures:**

**(H<sub>2</sub>O)<sub>3</sub>:**

$(H_2O)_3$:

1\1\FAU-CCC-SNODE075\Freq\RB3LYP\6-311+G(3df,2p)\H6O3\PUCHTA\28-Mar-20

08\0\\#P GEOM=ALLCHECK GUESS=READ SCRF=CHECK GENCHK RB3LYP/6-

311+G(3DF

,2P) FREQ\\3x H2O als 6-Eck\\0,1\O,-0.6840999131,-1.4629016025,0.12309

24985\O,1.6131530742,0.1330823853,-0.1227726555\O,-0.9348387235,1.3249

53207,-0.0718750469\H,0.0355131991,1.2382508614,-0.0495458024\H,-1.073

3173924,-0.5698790321,0.0742216235\H,1.0328265981,-0.6461228632,-0.038

5407288\H,-1.0615617459,-1.9582758914,-0.6081406783\H,2.2832079436,0.0

449132914,0.5591660633\H,-1.1703841033,1.9300417158,0.6352811543\\Vers

ion=IA32L-G03RevC.02\State=1-A\HF=-229.4139083\RMSD=9.556e-10\RMSF=7.7

16e-05\ZPE=45.8155278\Dipole=0.0258626,0.0369653,0.4502248\DipoleDeriv

4\Polar=29.9511688,-0.0370833,29.9092801,0.1414084,0.8960995,24.200270

8\PG=C01 [X(H6O3)]\NImag=0\\0.20436358,-0.07230074,0.57267253,0.191915

9848694,0.24847788,0.29036294\\0.00015762,-0.00016806,0.00013376,-0.00

44,-0.00002193,0.00008470,-0.00004632,0.00000776,-0.00002859\\\@

**$(H_2O)_4$ butterfly structure (up-down-up-down):**

1\1\FAU-CCC-SNODE024\Freq\RB3LYP\6-311+G(3df,2p)\H8O4\PUCHTA\26-Mar-20

08\0\\#P GEOM=ALLCHECK GUESS=READ SCRF=CHECK GENCHK RB3LYP/6-

311+G(3DF

,2P) FREQ\\(H2O)4 fuer Prof. Samiran Mitra\\0,1\O,-0.0540198723,-1.942

2876096,-0.012302025\O,1.9422876096,-0.0540198723,0.012302025\O,0.0540

198723,1.9422876096,-0.012302025\O,-1.9422876096,0.0540198723,0.012302

025\H,-0.7427786577,1.3670681695,-0.0100554256\H,-1.3670681695,-0.7427

786577,0.0100554256\H,0.7427786577,-1.3670681695,-0.0100554256\H,1.367

0681695,0.7427786577,0.0100554256\H,0.035797462,-2.5271094868,0.743994

4756\H,-0.035797462,2.5271094868,0.7439944756\H,2.5271094868,0.0357974

62,-0.7439944756\H,-2.5271094868,-0.035797462,-0.7439944756\\Version=I

A32L-G03RevC.02\State=1-A\HF=-305.896276\RMSD=5.551e-10\RMSF=1.139e-05

\ZPE=62.077341\Dipole=0.,0.,0.\DipoleDeriv=-0.8164229,-0.0375837,0.090

012,-0.0342634,0.2142648\Polar=40.8392894,0.0000001,40.8392891,0.,0.,3

2.0581663\PG=S04 [X(H8O4)]\NImag=0\\0.36055533,0.17704254,0.38418453,0

4,0.00004699,0.00001269,0.00005627,0.25804739,0.03680727,0.33173835\\-

642,0.00000234,-0.00001326,-0.00000642,-0.00000234,-0.00001326\\\@

**($H_2O$)$_4$ butterfly structure (up-up-up-down):**

1\1\FAU-CCC-SNODE064\Freq\RB3LYP\6-311+G(3df,2p)\H8O4\PUCHTA\18-Aug-20

08\0\\#P GEOM=ALLCHECK GUESS=READ SCRF=CHECK GENCHK RB3LYP/6-

311+G(3DF,2P) FREQ\\(H2O)4 fuer Prof. Samiran Mitra\\0,1\O,-0.0598693423,-1.943

8000892,0.0544025926\O,1.9481586979,-0.0511926939,-0.003080626\O,0.055

2710995,1.9438653825,0.0629325999\O,-1.9507872568,0.0634135849,0.02176

45872\H,-0.740690364,1.3680668343,0.0504072153\H,-1.3934947408,-0.7443

644615,0.0092617572\H,0.7467100913,-1.3858793559,0.0162009885\H,1.3670

024163,0.7406971351,0.0227008828\H,2.5665055026,0.0936985941,-0.722779

1273\H,-2.5374164596,0.0002029597,-0.7354754196\H,0.061919917,-2.64487

80377,-0.5893108337\H,-0.0127219495,2.4741668582,0.8608413074\\Version

=IA32L-G03RevC.02\State=1-A\HF=-305.8945898\RMSD=4.543e-09\RMSF=1.806e

-04\ZPE=61.807358\Dipole=0.0270756,-0.0782279,-0.8467201\DipoleDeriv=-

33,0.0027199,0.3067404,-0.028866,0.0329004,-0.0483793,0.2058512\Polar=

40.8128241,0.0216531,40.801704,0.1051131,1.2946705,32.0598991\PG=C01 [

X(H8O4)]\NImag=0\\0.37850347,0.15172579,0.46582265,-0.08239695,0.25951

-0.00000861,-0.02828004,0.24717496,0.36861487\\-0.00011671,-0.00001280

009356,0.00002795,0.00002079,0.00007319\\\@

**(H₂O)₄ butterfly structure (up -up-down-down):**

1\1\FAU-CCC-CCDH153\Freq\RB3LYP\6-311+G(3df,2p)\H8O4\PUCHTA\18-Aug-200

8\0\\#P Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/6-311+G(3df,

2p) Freq\\(H2O)4 up-up-down-down Freq:RB3LYP/6-311+G(3df,2p)\\0,1\O,1.

1548779165,1.565651119,0.0913107368\O,-1.5734283704,1.1444044966,0.098

6041644\O,-1.1540212938,-1.5649960208,-0.0948564553\O,1.5725213377,-1.

1486880157,-0.0952900906\H,-0.1720920569,-1.5618041325,-0.0871406895\H

,1.5419435876,-0.1682096894,-0.0477910347\H,0.1733497007,1.5642797772,

0.0717417483\H,-1.545272748,0.1645481075,0.0319308434\H,-2.1744140991,

1.4416220216,-0.5884755276\H,1.4390966364,2.1550139072,-0.611196034\H,

-1.4274430118,-2.1360962113,0.6267909527\H,2.1648364012,-1.4305473594,

0.6056023862\\Version=AM64L-G03RevD.02\State=1-A\HF=-305.8947498\RMSD=

3.266e-09\RMSF=1.671e-04\ZeroPoint=0.0986486\Thermal=0.108432\ZPE=61.9

029115\Dipole=0.0027922,0.0210959,0.0034259\DipoleDeriv=-0.841158,-0.0

0.2809704,-0.0140959,-0.070972,0.0072841,0.2211904\Polar=40.9699291,0.

0237704,40.9472853,0.0087557,-1.2545926,31.8114201\PG=C01 [X(H8O4)]\NI

mag=0\\0.54438432,0.08122429,0.25107878,-0.09146646,-0.25726600,0.3203

016810,0.24093792,-0.11591266,0.28529792\\0.00004511,0.00006263,0.0001

0.00002051,0.00001879,-0.00000597\\\@

**($H_2O$)$_5$:**

1\1\FAU-CCC-SNODE122\Freq\RB3LYP\6-311+G(3df,2p)\H10O5\PUCHTA\10-Apr-2

008\0\\#P GEOM=ALLCHECK GUESS=READ SCRF=CHECK GENCHK RB3LYP/6-

311+G(3D

F,2P) FREQ\\5 H2O IM 10ECK Freq:RB3LYP/6-311+G(3df,2p)\\0,1\O,-0.92941

21813,2.1248728803,0.0327919263\O,-2.3018813821,-0.2308889011,0.132919

8219\O,-0.4792758596,-2.2751872663,0.0590750998\O,2.0072293661,-1.1540

576585,0.0842123843\O,1.7189681165,1.5376998033,-0.2459427561\H,0.0328

267989,1.9489247499,-0.0800565208\H,-1.8335006557,0.6347227132,0.10125

77164\H,-1.1753239118,-1.5801665275,0.0601603894\H,1.1229917259,-1.586

9476273,0.0783168684\H,1.8601228455,0.5710596202,-0.1224398297\H,-1.00

49774214,2.6900109482,0.8054390259\H,-3.0351370832,-0.1587065997,-0.48

20814578\H,-0.6784731981,-2.8560111809,-0.6787115444\H,2.4408835755,-1

.4477878059,0.8889250177\H,2.1455628476,1.7653908484,-1.0752614737\\Ve

rsion=AM64L-G03RevC.02\State=1-A\HF=-382.3732898\RMSD=5.231e-09\RMSF=5

.041e-05\ZPE=77.5682151\Dipole=-0.0880726,-0.0254463,-0.3879425\Dipole

5076\Polar=51.5818039,0.0483068,51.4967415,-0.0656755,0.101681,40.2155

692\PG=C01 [X(H10O5)]\NImag=0\\0.48645163,-0.08194026,0.24050650,-0.06

0,-0.20469766,-0.11837464,0.40137311\\-0.00001246,0.00000023,-0.000041

0000015,0.00001076,-0.00002176,-0.00001789,0.00000027,0.00003274\\\@

**(H₂O)₆:**

1\1\FAU-CCC-SNODE121\Freq\RB3LYP\6-311+G(3df,2p)\H12O6\PUCHTA\30-Mar-2

008\0\\#P GEOM=ALLCHECK GUESS=READ SCRF=CHECK GENCHK RB3LYP/6-

311+G(3D

F,2P) FREQ\\6 H2O IM 12ECK\\0,1\O,0.0159943456,2.7052099849,0.13630825

17\O,-2.3507777423,-1.3387534828,0.1363082517\O,2.3347833967,-1.366456

5021,0.1363082517\O,-2.3347833967,1.3664565021,-0.1363082517\O,-0.0159

943456,-2.7052099849,-0.1363082517\O,2.3507777423,1.3387534828,-0.1363

082517\H,0.8541863529,2.1993350508,0.0315076339\H,-2.3317732019,-0.359

9204442,0.0315076339\H,1.477586849,-1.8394146066,0.0315076339\H,-1.477

586849,1.8394146066,-0.0315076339\H,-0.8541863529,-2.1993350508,-0.031

5076339\H,2.3317732019,0.3599204442,-0.0315076339\H,0.1193998346,3.225

1296917,0.9365871915\H,-2.8527441608,-1.5091615559,0.9365871915\H,2.73

33443262,-1.7159681358,0.9365871915\H,-2.7333443262,1.7159681358,-0.93

65871915\H,-0.1193998346,-3.2251296917,-0.9365871915\H,2.8527441608,1.

5091615559,-0.9365871915\\Version=AM64L-G03RevC.02\State=1-AG\HF=-458.

8499828\RMSD=6.365e-10\RMSF=7.708e-06\ZPE=93.2386556\Dipole=0.,0.,0.\D

542743,0.0483552,0.2683102,-0.0290008,0.0600523,-0.0077659,0.210368\Po

lar=61.9214569,-0.002459,61.9212931,-0.0000668,-0.0009046,48.6413477\P

G=S06 [X(H12O6)]\NImag=0\\0.40226316,-0.15618545,0.30073083,0.03141926

413243,-0.08695799,0.37383511\\0.00001396,0.00000651,0.00000580,-0.000

0.00000833,0.00000267\\\@